

INFRARED LASER-SPECIFIC REACTIONS INVOLVING BORON COMPOUNDS III: DECOMPOSITION OF PHOSGENE SENSITIZED BY BORON TRICHLORIDE

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Summary

The decomposition of phosgene initiated by boron trichloride under conditions of vibrational heating by a CO₂ laser has been studied. The reaction cannot be explained as a pure thermolysis but shows features of an infrared photosensitization.

1. Introduction

The present paper is part of an empirical study to explore the possibility of laser-specific product formation in reactions of polyatomic molecules (*cf.* ref. 1). Two reactions of this type have been found which seem to occur with a rather specific interaction of vibrationally excited boron trichloride. BCl₃ does not participate as a reaction partner but rather acts in the way of a catalyst. Upon vibrational heating by a continuous working CO₂ laser BCl₃ has been shown to cause the conversion of tetrachloroethylene to hexachlorobenzene [2] and the decomposition of phosgene according to the reaction COCl₂ → CO + Cl₂, as described in this paper. BCl₃ itself remains unattacked under these conditions. The product yield is (relatively) high in both cases. The process is well suited for the purification of crude BCl₃ which normally contains phosgene as an impurity.

2. Experimental

Mixtures of BCl₃ and COCl₂ at various pressure ratios were exposed to the radiation of the P(20) 00⁰1-10⁰0 CO₂ laser line (944.18 cm⁻¹). In some experiments other lines were also used (see later). The laser power was 6.0 ±

0.5 W. The experiments were conducted either with static gas or in a flow system. In the first case the reaction cell was a glass cylinder (l, 60 mm; i.d., 26 mm) with sodium chloride windows [2]. For the second case a flow apparatus was constructed which permitted the continuous control of the undecomposed COCl_2 . This flow reactor is made of glass. Details of the apparatus are given in Fig. 1. The reaction zone is located near the entrance window for the laser beam. The diameter of the inner tube is 6.5 mm. The length of the reaction zone is visible because of the BCl_3 luminescence [3]. It measures 5 mm for a laser power of 6 W and a BCl_3 pressure of 120 Torr. For a flow rate of 0.5 mm s^{-1} the residence time of an admixture of COCl_2 and BCl_3 in the reactive volume is about 5 s. Under these conditions the decomposition of COCl_2 at a partial pressure of 35 Torr was 91% complete in one run. Next to the reaction volume is an IR absorption cell which can be placed in the probe beam of a spectrometer to permit analysis for BCl_3 (990 cm^{-1}), COCl_2 (1850 cm^{-1}) and CO (2160 cm^{-1}) contents. These absorptions can easily be calibrated to give the absolute concentrations of the gases. BCl_3 and Cl_2 are subsequently removed from the mixture by condensation in a trap cooled in liquid oxygen and can be further separated by distillation. By cyclic operation of this system the phosgene content was reduced below the limit of infrared detection (0.01 Torr COCl_2 produces 1% absorption at 1820 cm^{-1} with a 10 cm absorbing length). For comparison under static conditions in a mixture of $\text{BCl}_3 + \text{COCl}_2 = (170 + 15)$ Torr the conversion of phosgene was found to be 99.8% within 2 min. The remaining COCl_2 content could then still be reduced by further irradiation.

3. Results and discussion

The range of pressures investigated was 30 - 300 Torr BCl_3 and 0.02 - 300 Torr COCl_2 . The products were examined using IR spectroscopy and mass spectrometry and in addition for the Cl_2 formed using its UV absorp-

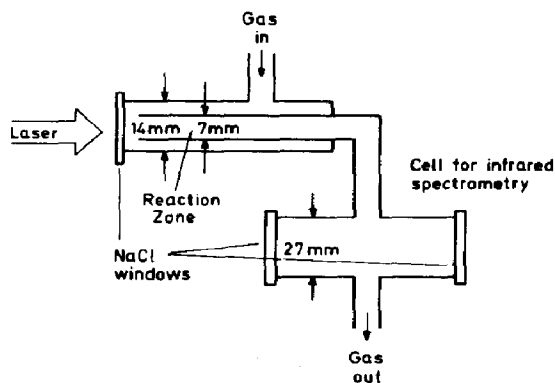


Fig. 1. Flow cell for the BCl_3 -sensitized decomposition of COCl_2 .

tion. In all cases the only products were Cl_2 and CO . The pressure changes for BCl_3 were negligible. COCl_2 [4] alone did not yield noticeable amounts of dissociation products with irradiation by either the P(20) (944.18 cm^{-1}) or the P(50) (1016.72 cm^{-1}) line.

Figure 2 shows that the observed effect exhibits a threshold behaviour for the laser power. Effective decomposition occurs only at a power exceeding 2.5 W. These data as well as the results shown in Figs. 3 and 4 were obtained in a static gas mixture. Figure 3 demonstrates that the dissociation of 1 Torr of COCl_2 goes to completion in 20 s if BCl_3 is present at 100 Torr. Such a situation may be considered to be typical for applications of this process to the purification of crude (COCl_2 contaminated) BCl_3 . Figure 4 gives

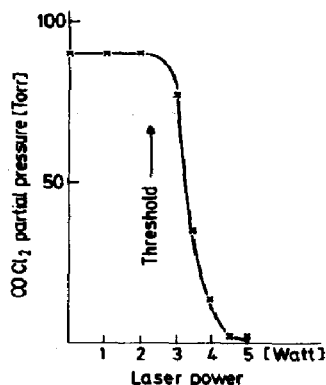


Fig. 2. Dependence of COCl_2 decomposition on the laser power (time of irradiation, 2 min; 150 Torr BCl_3).

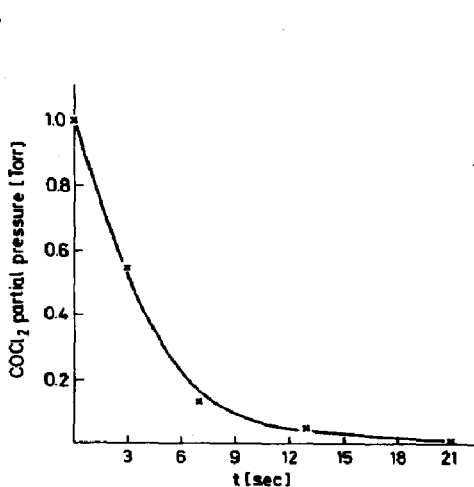


Fig. 3. Dependence of COCl_2 decomposition on the time of irradiation (100 Torr BCl_3).

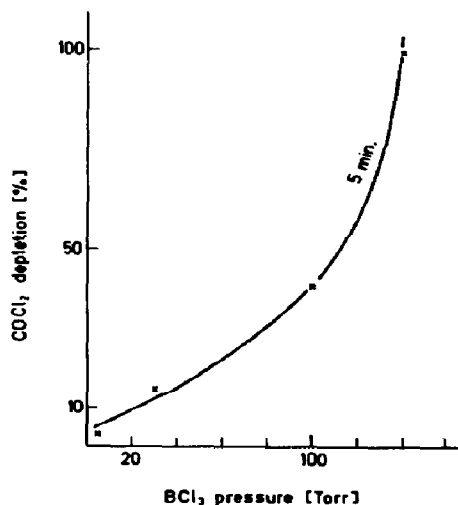


Fig. 4. Dependence of COCl_2 decomposition rate on BCl_3 pressure (time of irradiation, 5 min; initial COCl_2 pressure, 300 Torr).

the yields of COCl_2 conversion as a function of the BCl_3 pressure. Thus, at 140 Torr of BCl_3 as much as 300 Torr of COCl_2 can be removed from a mixture within 5 min. This gives a rough indication of the overall quantum yield Φ_{max} for this decomposition process which is estimated from Fig. 4 to be about 0.3%.

The most important question which arises is that of the thermal or non-thermal nature of the process. In our opinion there are several arguments in favour of the second interpretation.

(1) The non-catalyzed pyrolysis of COCl_2 requires temperatures of about 1000 °C [5]. The effective gas temperature, although not exactly known because of possible spatial variations, can never be so high particularly for the flow system used here which has good gas-wall contact and for the BCl_3 -lean mixtures used in Fig. 4. The rise in the equilibrium gas temperature was indeed negligible even after hours of irradiation.

(2) In contrast, visible luminescence of BCl_3 is observed which points to BCl_3 dissociation [6]. This is a reversible process and no net loss of BCl_3 is found. It is conceivable then that vibrational energy transfer from highly excited BCl_3 is the cause of the COCl_2 decomposition. Since the dissociation energy of phosgene ($\Delta H_{298} = 77.3 \pm 3 \text{ kcal mol}^{-1}$) is smaller than that of BCl_3 ($\Delta H_{300} = 105 \text{ kcal mol}^{-1}$) the dissociation of COCl_2 molecules appears to be possible even if only part of the energy that can mainly be stored in BCl_3 vibrations is transferred.

(3) The very steep threshold observed (*cf.* Fig. 2) is more typical for multiple photon laser excitation than for thermal decomposition.

(4) As an alternative explanation to the vibrational energy transfer proposed under (2) a specific (catalytic?) action of the BCl_3 dissociation fragments (Cl , BCl_2) should be invoked. This cannot be ruled out at present by the experimental evidence. There is no indication of any formation of a complex between COCl_2 and BCl_3 itself at least for the unexcited molecules [7].

(5) If BCl_3 acts only as a heat bath it ought to be possible to replace it by other molecules that have high absorption coefficients for CO_2 laser radiation. However, when SF_6 ($\text{SF}_6 + \text{COCl}_2 = (210 + 18) \text{ Torr}$) was tried for this purpose only 17% COCl_2 decomposition was observed under conditions where decomposition was essentially quantitative with BCl_3 . In this case the P(24) line of the CO_2 laser at 940.52 cm^{-1} was used. This is consistent with the results from a rather careful study of homogeneous laser pyrolysis of many molecules using SF_6 as a heat bath by Shaub and Bauer [8]. In this study COCl_2 was not tried but molecules with similar dissociation energies showed only small dissociation yields even for higher laser powers than that used in this work. It was also demonstrated that SF_6 itself does not dissociate under these conditions. Its decomposition requires equilibrium temperatures exceeding 1600 K [8].

It is worth pointing out that the reaction just described can be utilized for the purification of industrial BCl_3 which usually contains COCl_2 . For this mixture purification by simple distillation is difficult since the boiling points

of the two compounds differ only by 4 °C. Purification can then be accomplished by adsorption [9] at lower temperatures or by catalytic decomposition [3, 10] at high temperatures. Periodic regeneration or replacement of the catalysts or adsorbers becomes necessary. In contrast the process described here is continuous without the need for heating or cooling of the gas.

In conclusion we believe that we have shown that vibrationally excited boron trichloride or a fragmentation product of this molecule can be used to dissociate phosgene specifically. The reaction cannot be solely a result of equilibrium heating of the gas. It is thus suggested that this decomposition reaction constitutes an example of a new type of reaction which may be described as IR photosensitization.

Note

After submission of this paper results were published by Merritt and Robertson [11] which are related to the data reported here, although considerably different experimental conditions were used.

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